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A review on conventional technologies and emerging process intensification (PI) methods for biodiesel production

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ABSTRACT

Biodiesel is commonly produced from lipid feedstock, animal fats and waste cooking oil by transesterification reaction. Considering the depletion of fossil fuel, biodiesel is gaining more attention as a renewable and environmental friendly fuel. The rapid growth of biodiesel industry thereafter has raised concerns to many existing commercial biodiesel enterprises. The major issues like feedstock flexibility, yield productivity and environmental impact are always the challenges to the continuous growth of conventional biodiesel processing technology. The processing of biodiesel is greatly hinged on the rich scientific background and technology development for better process advancement. The present paper reviews various concerns raised from the commercial biodiesel processing technology. It also addresses some innovative process intensification (PI) technologies, which likely bring appropriate technological improvement for biodiesel production.

Contents

1. Introduction

1.1. Renewable fuel—biodiesel

The ever-increasing global population and the importance of limiting global warming have led to increased awareness of the

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needs for energy and the requirements for reducing global climate change. Biofuel, a renewable and environmental-friendly fuel developed as an alternative to fossil fuels, has been gaining prominence in recent years. On a global basis, the use of renewable biofuels (transport fuels derived from biomass feedstock) is expected to increase rapidly over the next decades. Biodiesel, the first-generation biofuel, is generally produced from a variety of renewable lipids such as virgin vegetable oils, waste vegetable oils, animal fats and non-edible oils. Biodiesel has similar physicochemical properties as the diesel produced from crude oil, and it can be used directly in the diesel engine [1]. The use of biodiesel not only will leverage the use of fossil fuels, it could greatly reduce greenhouse gas emissions. It also helps to reduce the emission level of some pollutants.

1.2. Standard specification for biodiesel

As biodiesel is gaining its recognition as an alternate fuel, standards and regulatory compliance are mandatory for its commercialisation and market introduction. There are two major biodiesel standards that are most referred to, namely, the American Standard Specifications for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels, ASTM D6751 and the European Standard for Biodiesel, EN 14214. Both the standards are summarised in Tables 1 and 2, respectively. Most of the parameters specified in both the standards are similar or very close. The major differences between these standards are their intended applications and the preferred test methods published by European Committee for Standardization (CEN) and American Society for Testing and Materials, respectively. The EN 14214 sets the specifications and test methods for biodiesel to be used as automotive fuel for diesel engines, in conformation with the European Automotive Diesel Standard (EN 590) while the US ASTM D6751 specifies the standards for biodiesel (100%) for use as a blend component with diesel fuels [2]. In order to give a quality assurance to the users, the biodiesel produced must meet the specification of ASTM D6751 and EN 14214 so that it can be used directly to run the existing diesel engines without major modifications or as a biodiesel blended with petrol diesel to create less hazardous emissions.

1.3. Raw materials used for commercial biodiesel production

The type and availability of feedstock, production method, additives used and operational costs are contributed to the cost of biodiesel production [5]. Among these many factors, raw materials contribute to the major portion in the biodiesel production cost [89]. Selection of raw materials mainly depends on its availability (regional production and productivity), cost and characteristics of oil (stability and cold flow properties). Countries such as United States of America (USA) and those belonging to European community are self-dependent in production of edible oils and even have a surplus amount to export [6]. Therefore, edible oils such as soybean and rapeseed are commonly used to produce biodiesel in USA and European Nations, respectively. Similarly, leading Asian countries such as Malaysia and Philippines are utilising edible oils such as palm oil and coconut oil respectively for biodiesel production. However, the main raw material used in India is a non-edible and an unutilized material, *Jatropha curcas* (Jatropha) owing to its insufficient edible oils' production [86]. Table 3 shows the common raw materials used in various countries to produce biodiesel and their oil yield per hectare per annum.

The oil yield data in Table 3 indicates that oil palm in Malaysia can produce up to 3.93 tonnes of crude oil per hectare per year, whereas, the other oilseeds are only able to produce less than 1.5 tonnes per hectare per year. Highest yield promises that palm oil is the most feasible and economical oil to be used for commercial biodiesel production. Search for a raw material for biodiesel production is not confined to vegetable oils only. There

Table 1
ASTM D6751-11a specifications for B-100 biodiesel.
Source: [3].

Property	ASTM method	Limits	Units
Calcium and magnesium, combined	EN14538	5 max.	ppm (μg/g)
Flash point (closed cup)	**D93**	**93 min.**	**°C**
Alcohol control (one to be met)			
1. Methanol content	EN14110	0.2 max.	mass %
2. Flash point	D93	130 min.	°C
Water and sediment	**D2790**	**0.05 max.**	**% vol**
Kinematic viscosity, 40°C	D445	1.9–6.0	mm^2/sec
Sulfated ash	D874	0.02 max.	% mass
Sulphur			
S 15 Grade	**D5453**	**0.0015 max. (15)**	**% mass (ppm)**
S 500 Grade	**D5453**	**0.05 max. (500)**	**% mass (ppm)**
Copper Strip Corrosion	D130	No. 3 max.	
Cetane	D613	47 min.	
Cloud point	**D2500**	**Report**	**°C**
Carbon residue 100% sample	D4530[a]	0.05 max.	% mass
Acid number	**D664**	**0.5 max.**	**mg KOH/g**
Free glycerine	**D6584**	**0.020 max.**	**% mass**
Total glycerine	**D6584**	**0.240 max.**	**% mass**
Phophorus content	D4951	0.001 max.	% mass
Distillation	D1160	360 max.	°C
Sodium/potassium, combined	EN14538	5 max.	ppm (μg/g)
Oxidation stability	**EN15751**	**3 min.**	**Hours**
Cold soak filtration	**D7501**	**360 max.**	**Seconds**
For use in temperature below −12 °C	**D7501**	**200 max.**	**Seconds**

Bold Font BQ-9000 **Critical Specification Testing** Once **Production Process Under Control.**

[a] The carbon residue shall be run on the 100% sample.

Table 2
EN 14214 quality standards. *Source*: [4].

Parameter	Method	DIN EN14214		
		Minimum	Maximum	Unit
Ester	DIN EN 14103	96.5	–	% (m/m)
Density 5 °C	DIN EN ISO 12185	860	900	kg/m^3
Viscosity 40 °C	DIN EN ISO 3104	3.5	5.0	mm^2/s
Flash point	DIN EN ISO 3679	120	–	°C
CFPP	DIN EN 116	–	–	°C
Sulphur	DIN EN ISO 20884	–	10.0	mg/kg
Organic matter (10%)	DIN EN ISO 10370	–	0.3	% (m/m)
Octane	IP 498	51.0	–	–
Sulphur ash	ISO 3987	–	0.02	% (m/m)
Water	DIN EN ISO 12937	–	500	mg/kg
Total contamination	DIN EN ISO 2160	–	24	mg/kg
Copper corrosion	DIN EN ISO 2160	1	1	grad corrosion
Oxidation stability (110 °C)	DIN EN 14112	6.0	–	h
Acid number	DIN EN 14104	–	0.5	mg KOH/g
Iodine number	DIN EN 14111	–	120	g iod/100g
Linolenic acid methyl-ester	DIN EN 14103	–	12.0	% (m/m)
Methanol	DIN EN 14110	–	0.20	% (m/m)
Free glycerol		–	0.020	% (m/m)
Mono-glycerides		–	0.80	% (m/m)
Di-glycerides	DIN EN 14105	–	0.20	% (m/m)
Triglycerides		–	0.20	% (m/m)
Total glycerol		–	0.25	% (m/m)
Phosphor	DIN EN 14107	–	10.0	–
Metals I (Na+K)		–	5.0	–
Metals II (Ca+Mg)	DIN EN 14538	–	5.0	–

Table 3
Common raw materials used for biodiesel production and their oil yield. *Source*: [8].

Oilseeds	Oil yield (tonne/ha/yr)
Palm Oil (Malaysia)	3.93
Rapeseed (EU)	1.33
Soybean (USA)	0.46
Sunflower (Argentina)	0.66
Jatropha (India)	1.44
Coconut (Philippines)	0.66

Table 4
Conventional and non-conventional feedstocks used for the biodiesel production. *Source*: [88].

Conventional feedstocks		Non-conventional feedstocks
Mahua	Soybeans	Lard
Piqui	Rapeseed	Tallow
Palm	Canola	Poultry fat
Karang	Babassu	Fish oil
Tobacco seed	Brassica carinata	Bacteria
Rubber plant	Brassica napus	Algae
Rice bran	Copra	Fungi
Sesame	Groundnut	Micro algae
Safflower	Cynaracardunculus	Tarpenes
Barley	Cotton seed	Latexes
Coconut	Jatropha nana	Microalgae
Laurel	Jojoba oil	
Used cooking oil	Pongamiaglabra	

are many options for utilising different feedstock types for biodiesel production. According to Shahid and Jamal reported that there are more than 300 feedstocks could be used to produce biodiesel [88]. They have been categorised as the conventional and non-conventional feedstocks used for the biodiesel production in Table 4. Besides the vegetable oils as mentioned in Table 3, microalgae, animal fats and waste vegetable oils also provide viable feedstock opportunities for biodiesel production [7,87]. However, the latter mentioned feedstock types are not yet commercially used for biodiesel production.

1.4. Transesterification reaction

Though vegetable oil could be used directly as an engine fuel, the high viscosity of vegetable oils should be reduced before being used in common diesel engines. Rudolf Diesel (1858–1913) tested vegetable oils as fuel on his extraordinary engine [9], [78]. From a technical point of view, high viscosity of vegetable oils causes poor atomisation of the fuel in the engine's combustion chambers and eventually results in operational problems, such as engine deposits [10,79,80]. Solutions to the viscosity problem have been addressed in at least four possible ways: dilution of vegetable oils, micro-emulsion of oils, pyrolysis and transesterification of oils and fats [11,81,82]. Dilution, micro-emulsion and pyrolysis are the approaches that account for a significant amount of the literature in historic times but appear to have received little attention after transesterification being widely developed and adopted to produce a cleaner and environmentally safe fuel. Hanifa et al. [83] mentioned that pyrolysis and micro-emulsion are costly methods which yield low quality biodiesel compare to transesterification method.

The transesterification of vegetable oils ensures the quality of biodiesel by lowering its viscosity and enhancing other physicochemical properties [12]. In the biodiesel industry, transesterification is a universal and established method for biodiesel production. In the presence of acid or base catalyst, triglycerides (TG) in oil or fats reacts with commonly used alcohol, methanol (MEOH), to produce biodiesel, which is also known as fatty acid methyl ester (FAME), and release glycerol (GLY) [13,18,80,84,85]. As transesterification consists of a number of consecutive

and reversible reactions [11,14], the TG is converted stepwise into diglycerides (DG), monoglycerides (MG) and finally GLY, whereby a mole of FAME is liberated at each step. The mechanism of transesterification reaction is presented in equation

$$\underset{\text{Triglyceride}}{\begin{matrix} CH_2COOR_1 \\ | \\ CH_2COOR_2 \\ | \\ CH_2COOR_3 \end{matrix}} + \underset{\text{Alcohol}}{R'OH} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \underset{\text{Diglyceride}}{\begin{matrix} CH_2OH \\ | \\ CH_2COOR_2 \\ | \\ CH_2COOR_3 \end{matrix}} + \underset{\text{Alkyl ester}}{R'COOR_1} \quad (1)$$

$$\underset{\text{Diglyceride}}{\begin{matrix} CH_2OH \\ | \\ CH_2COOR_2 \\ | \\ CH_2COOR_3 \end{matrix}} + \underset{\text{Alcohol}}{R'OH} \underset{k_4}{\overset{k_3}{\rightleftarrows}} \underset{\text{Monoglyceride}}{\begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2COOR_3 \end{matrix}} + \underset{\text{Alkyl ester}}{R'COOR_2} \quad (2)$$

$$\underset{\text{Monoglyceride}}{\begin{matrix} CH_2OH \\ | \\ CH_2OH \\ | \\ CH_2COOR_3 \end{matrix}} + \underset{\text{Alcohol}}{R'OH} \underset{k_6}{\overset{k_5}{\rightleftarrows}} \underset{\text{Glycerol}}{\begin{matrix} CH_2OH \\ | \\ CH_2OH \\ | \\ CH_2OH \end{matrix}} + \underset{\text{Alkyl ester}}{R'COOR_3} \quad (3)$$

During transesterification reaction, oils, MEOH and FAME are partially miscible [15]. Thus, the reaction mixture passes from a biphasic (MEOH phase and oil phase) system to another biphasic (FAME-rich phase and GLY-rich phase) system, probably via an emulsion [16]. This results in a two-phase reaction causing a mass-transfer limitation for effective reaction. Furthermore, owing to the final products (FAME & GLY) exist in two separate phases; the desired products must be separated via several purification and separation steps. In order to achieve efficient transesterification reaction, a homogeneous reaction to get high conversion and heterogeneous separation to obtain high purity of biodiesel, which is free from TG to meet the stringent ASTM D6751 and EN14214 standards, must be obtained.

Through extensive research, many commercial enterprises have offered comprehensive, innovative and state-of-the-art technologies to produce high-quality biodiesel consistently at a competitive price via transesterification process. Nevertheless, there are several issues in commercial biodiesel production need to be resolved, and it will be discussed later in the paper. Building a sustainable biodiesel industry, extra efforts are still required in the research and development of biodiesel production by developing a robust technology to produce, refine and recover the valuable end products. In order to thoroughly understand the development of biodiesel production technology, it is indeed important to review the conventional technologies as well as to have an understanding of the recent advances in biodiesel production technology. Therefore, this paper gives a critical review on the conventional biodiesel production technologies as well as detail knowledge of the recent emerged process intensification (PI) technologies for biodiesel production, which have been experimentally proven to be far better than the conventional technologies.

2. The challenges faced by conventional technologies

Several commercial technologies for biodiesel production have been developed and widely adopted. At present, the majority of biodiesel plants are operated either in batch or continuous mode using conventional homogeneous acid or alkali-based transesterification conversion technology. In homogeneous catalysis, alkali-catalyst is much suited for the transesterification of vegetable oils because the process proceeds much rapid than the acid-catalysed reaction whereby acid-catalyst is usually used for the esterification of free fatty acid (FFA). Due to the fact that the alkali-catalysts are less corrosive than acid catalysts, the alkali-catalysts such as sodium hydroxides (NaOH), sodium methylate, alkali metal alkoxides [17,18] and sodium or potassium carbonates [19] are usually a preferred choice in industrial processes.

2.1. Feedstock flexibility

To date, high cost of biodiesel still remains as the major barrier to commercialisation when compared to petroleum-based diesel fuel. It is reported that approximately 70–95% of the total biodiesel production cost arises mainly from the cost of feedstocks [20]. In consideration of the profit, biodiesel plants must be able to respond to availability and market fluctuations in the price of various feedstocks. Therefore, many commercial biodiesel enterprises have claimed multi-feedstock flexibility in their biodiesel production systems. Some companies such as Pacific Biodiesel, Lurgi and Desmet Ballestra claimed that animal fats, used oils and greases with high content of FFA can be used in the respective biodiesel processes. However, pre-treatment and/or esterification units are actually required to reduce the content of FFA in the feedstock.

It is reported that these companies are using alkali catalyst in stages of process producing biodiesel. Without pre-treatment steps, the presence of FFA in the alkali-catalysed biodiesel process will promote soap formation. According to Freedman et al. [18], the soap formed partially consumes the catalyst, reduces products yield and interferes with the separation of glycerol. Therefore, a pre-treatment or esterification step becomes crucial in the biodiesel reaction when feedstock with high content of FFA is used. With the pre-treatment unit, Pacific Biodiesel's unique reaction technologies allow the use of feedstock with FFA content up to 15% without loss of yield [21]. However, Desmet Ballestra's technology [22] is only able to process used frying oil with a maximum 5% of FFA by employing an acid-catalysed pre-esterification to remove excess FFA.

Study shows that the alkali-catalysed process using virgin vegetable oil has the lowest capital investment cost. However, the cost of using virgin oil leads to a higher total manufacturing cost [20]. Instead of using virgin vegetable oils, the conventional industrial biodiesel processes as mentioned above use waste oils in the alkali-catalysed process. Still, the cost associated with the feedstock pre-treatment step, eventually, offset the cost savings from using used oils or waste oils.

Aside from alkali-catalysed processes employed by the above commercial biodiesel enterprises, a heterogeneous catalyst process has been developed by the French Institute of Petroleum (IFP) and commercialised by the Axens Technologies. In Axen's Esterfip-H process, a completely heterogeneous catalyst, which consists of a spinal mixed oxide of zinc and aluminium (zinc aluminate), is used to produce biodiesel [23,24]. The use of heterogeneous catalyst in the process produces a higher quality of biodiesel and glycerol as well as eases the products' separation. Nevertheless, the feedstock must have a FFA content of not exceeding 0.25% and water content must be lower than 1000 ppm [24]. This drawback has set a limitation on the feedstock selection, either virgin or refined vegetable oil, when using Axen's Esterfip-H technology to produce biodiesel.

2.2. Products quality and yield efficiency

The most common system for producing biodiesel through transesterification reaction is using a batch, stirred tank reactor. Transesterification is a reversible reaction; therefore, complete conversion and high yield can hardly be achieved in a single-step process without removing the reaction products such as FAME and GLY. Recently, the use of continuous stirred tank reactor (CSTRs) has become a popular variation of the batch process. Research finding shows that a biodiesel system with two reactors in series, whereby the glycerine is removed from the first reactor before feeding to the second reactor, gives better product purity and operating cost than with a single reactor [25]. The CSTRs can vary in volume to allow for a longer residence time for the first CSTR, to allow the first CSTR to operate at a higher reactant concentration and a higher reaction rate, and therefore, to achieve a greater extent of reaction.

Pacific Biodiesel reported that their biodiesel plants utilise a waterless semi-batch process which combines the advantages of batch and continuous processes into a single process whereby the biodiesel production is performed in batch for easy feedstock blending, efficient chemical loading, and quality control [26]. Pacific Biodiesel's three-stage product refining produces a fuel quality meeting ASTM D6751-07a standards, while the vacuum distillation and dry refining steps remove trace amounts of water, MeOH and minor impurities. The by-product refining technology allows the recovery of GLY at the purity of more than 85% from the crude by-product stream. The resulting GLY is upgradeable to United States Pharmacopia (USP) quality, but additional cost of purification step will be incurred. In addition, the process is designed to recycle every drop of feedstock diverted in the production process and sized to ensure consistent output. Though the biodiesel produced is compliance with ASTM D6751-07a and recycling feedstock into the process improves the yield, the complete conversion of oil and the yield productivity of this semi-batch transesterification reaction are still questionable.

Lurgi and Desmet Ballestra biodiesel enterprises claimed that the yield of the continuous transesterification reaction can achieve as high as 100% and 99.8%, respectively, while both the biodiesel products are meeting the latest and most stringent European and/or US ASTM standards specifications [22,27]. The unique feature of Desmet Ballestra continuous transesterification process allows the continuous separation of the GLY phase from the reaction mixture within each of the three reaction steps. Lurgi's biodiesel technology allows transesterification reaction takes place in a two-stage mixer-settler unit, while the subsequent settling section allows for the separation of biodiesel as the light phase from GLY as the heavy phase. Both the reaction technologies allow shifting the reaction equilibrium towards the products, and therefore, maximising the yield and minimising the catalyst consumption. In addition, Lurgi and Desmet Ballestra purification steps for the heavy or lower GLY phase produce crude GLY with final concentration up to $>80\%$ and 88–90%, respectively. This crude GLY products can be sent to further GLY purification steps to produce the Pharmaceutical-grade GLY meeting EU Pharmacopeia standard 99.5. However, this incurs a cost of running additional GLY purification steps to the total manufacturing costs.

On the other hand, Axens' Esterfip-H biodiesel technology involves a continuous heterogeneous catalytic transesterification reaction whereby the catalyst section includes two fixed bed reactors that are fed by oil and MeOH [28]. The complete conversion is reached within two successive fixed-bed reactor stages, with glycerol separated to shift the equilibrium towards the products [29]. The Axens' Esterfip-H biodiesel technology is more favourable than the other technologies because it can produce biodiesel of higher purity exceeds 99% with the yield close to 100% at the first instance without purification step to remove water and residual catalytic materials. In addition, GLY can be directly produced at a high level of purity, at least 98%, and free of contaminants. These aspects eliminate the products purification and refining steps, and ultimately, reduce the total manufacturing costs.

2.3. Environmental impact

Another issue that plagues biodiesel production is the removal of catalyst residues, residual of TG, free glycerine and other undesirable products soluble in the biodiesel. Proper removing and handling of these impurities are the important aspects to achieve environmental sustainability. Karaosmanoglus et al. [30] studied three biodiesel refining methods such as washing with hot distilled water, washing with water and petroleum ether and neutralisation with sulphuric acid (1:1). The results show that the best refining method is washing with distilled hot water at 50 °C on the basis of biodiesel purity and refining costs. The Lurgi's biodiesel technology as discussed earlier is based on transesterification reaction of TG with MeOH to form FAME and GLY in the presence of an alkaline catalyst. At the end of the reaction, the mixture is neutralised by adding hydrochloric acid solution. A subsequent counter-current washing step removes by-product components and gives a "ready for use" biodiesel after final drying step [27]. It is highlighted that biodiesel refining step is done within a closed wash-water loop. However, the water consumption is approximately 20 kg for the production of one ton of rapeseed methyl ester. The surplus MeOH contained in the GLY water is removed in a rectification column and used as a recycle stream to the process.

According to the Desmet Ballestra [22], the transesterification reaction is accomplished in three steps with a MeOH surplus with respect to the stoichiometry quantity, and uses an alkali methylate in anhydrous MeOH solution as a catalyst. Purification of the methyl ester (biodiesel) phase involves separation of unreacted MeOH, washing with citric acid and water solutions and final drying. Prior to the methyl ester washing step, the unreacted MeOH is recycled back directly to the transesterification unit. The soap formed and water phase leaving the washing step of the residual GLY are recycled back to the GLY purification unit. At the final methyl ester drying section, the separated wet MeOH is sent to the rectification unit, to recover the excess MeOH for subsequent transesterification. Though it did not mention about the water consumption for the entire production line, there is waste water generated from the biodiesel plant due to the water washing refining step. Even though clean biodiesel is produced from both the commercial biodiesel enterprises (Lurgi and Desmet Ballestra), yet, more waste water is produced and required to be treated intensively before discharge. This, eventually, has led to cost disadvantage in the biodiesel production. Careful attention is needed to enhance the refining step and create conditions that maintain high product quality as well as assure the environment quality.

Pacific Biodiesel's biodiesel production systems utilise a waterless semi-batch process whereby a dried and filtered feedstock is reacted with MeOH using a hydroxide catalyst in a two-stage process to yield FAME [21]. After removal of co-product (GLY), the crude methyl ester is vacuum distilled to remove excess MeOH. Then, the methyl ester is treated through the dry refining process to remove catalyst residues, free glycerine, and other impurities in the methyl ester. Dry refining process is a unique biodiesel refining technology, developed by Pacific Biodiesel that uses "no water washing" concept but yet provides consistently high fuel quality. In addition, the use of a three-step recovery system keeps MeOH consumption to the theoretical minimum. Complete MeOH

recovery reducing loss of MeOH and leading to cost saving. The dry refining process which employs "use no water" concept reduces hazardous waste water and resolves waste treatment problem.

On the other hand, in Axen's Esterfip-H heterogeneous catalytic process consists of two fixed bed reactors; excess MeOH is removed after each reactor by partial evaporation [28]. Following the partial evaporation, the FAME and GLY are separated in a settler whereby GLY outputs are gathered, and the residual MeOH is removed by evaporation. Excess MeOH removed by evaporation is recycled and mixed with the fresh MeOH [24]. Biodiesel is recovered after the final MeOH vaporisation under vacuum followed by a final purification in an absorber for removing the soluble GLY. The Axen's Esterfip-H technology involves no hazardous chemical handling and minimal waste generation. Nevertheless, the main drawback of Axen's Esterfip-H process is that the system must be performed at higher temperature and pressure than other commercial biodiesel processes, with a higher MeOH to oil ratio. Though the operating condition is not clearly mentioned in Axen's Esterfip-H process specification, higher operating temperature and pressure definitely lead to high operational costs compared to other commercial biodiesel processes, which normally operate at standard conditions of 60 °C and atmospheric pressure.

2.4. Remarks on the challenges faced by conventional technologies

The conventional continuous transesterification processes as discussed earlier need longer residence time, resulting in increasing reactor volume, high capital cost, large "footprint" and difficult to control. The presence of FFA and water in the feedstock causes soap formation as a by-product of the reaction. Soap formation causes a reduction in reaction yield and loss of biodiesel product via entrainment in the soap phase during the washing process. If feedstock with a high percentage of FFA is used, an energy extensive feedstock pre-treatment is required prior to the transesterification reaction. Another concern is regarding the removal of residual TG and GLY from the biodiesel product. Due to transesterification is an equilibrium reaction, it is difficult to drive the reaction to complete conversion of the TG, and thus products refining process is necessary. The post-treatment of the products, by-products and wastes not only will give rise to a challenging wastewater treatment problem but also incur significant manufacturing costs. Besides, owing to immiscibility of oils and MeOH, the two-phase transesterification reaction will cause mass-transfer limitation in the process.

3. Process intensification methods

Considering the current drawbacks in conventional biodiesel production technologies, new technologies have been developed by the collaboration of many researchers and industries based on process intensification (PI) approach. One of the pioneers defined PI as a term used to describe the strategy of reducing the size of chemical plant needed to achieve a given production objective [31]. However, Stankiewicz and Moulijn [32] have a different point of view in defining PI. They proposed: "Any chemical engineering development that leads to a substantially smaller, cleaner, and more energy-efficient technology is PI". According to Stankiewicz and Drinkenburg [33], PI could improve yield or selectivity and facilitate separation, thus resulting in a lower investment cost, smaller inventory (safety aspects), and improved heat management/energy utilisation.

The whole idea of PI can be generally classified as process-intensifying equipment and process-intensifying methods as shown in Fig. 1. The biodiesel production technologies developed based on the PI concept focus on shorter reaction time but high conversion, low molar ratio of alcohol to oil, low catalyst concentration and most importantly, lower operating cost and energy consumption for biodiesel purification, and recovery of glycerol, catalyst and excess alcohol. Furthermore, these technologies also allow feedstock flexibility and rapid reaction permitting continuous production and separation of the reaction products. Eventually, this gives efficient recovery of catalyst, high product yield and quality as well as a reduction in environmental impact.

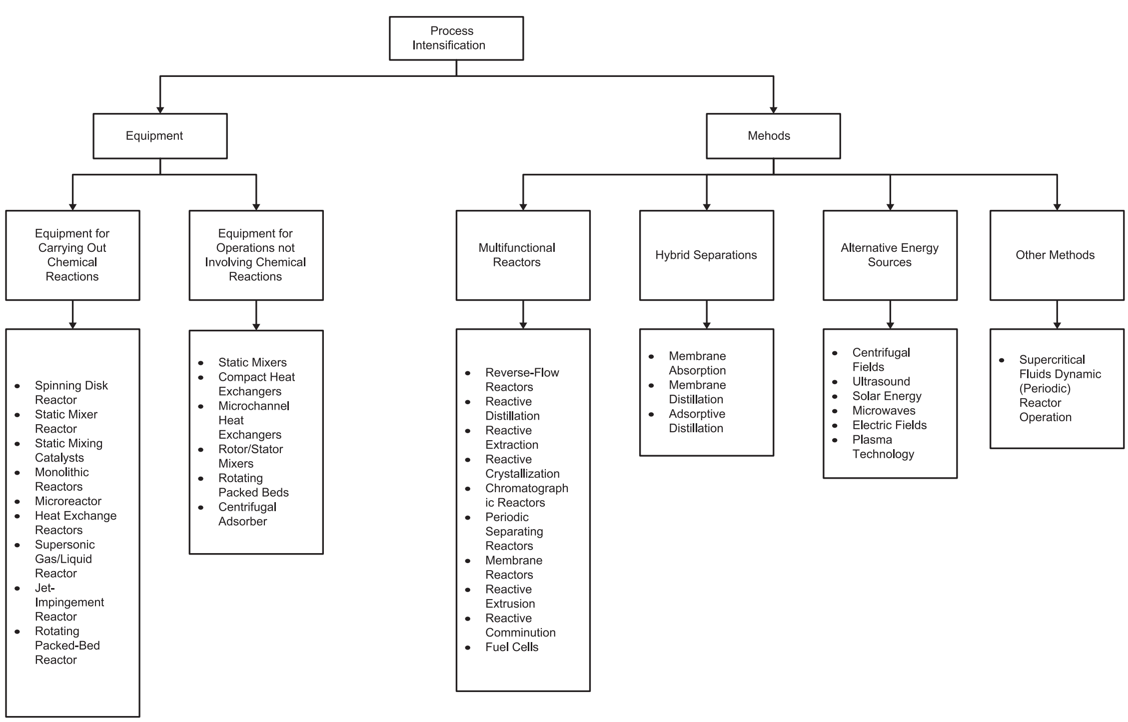


Fig. 1. Process intensification in terms of equipment and methods [32].

3.1. Reactive distillation column

The reactive distillation (RD) is a hybrid process that combines the chemical reaction and product separations in a single unit. More specifically, RD is the process in which chemical reaction and distillation separation are carried out simultaneously within a fractional distillation apparatus [34]. The main purpose or advantage of a RD column is the separation of reactants and products to boost the conversion and to improve the selectivity by breaking the reaction equilibrium restrictions [35,36]. Along with these promised advantages, extensive works have been done to explore the biodiesel production by using RD system [36–43].

A novel reactor system using RD, as shown in Fig. 2, was developed and investigated by He et al. [44] for biodiesel production from canola oil and MeOH. The feed passed through an in-line static mixer and entered into the RD column near the top. The reactant mixture flowed downward from the top of the RD column across the plate while the MeOH vapour (vaporised from the product mixture in the reboiler) flowed upward to provide uniform mixing at each plate. This made the reaction zone of the RD column consisted virtually of a series of “mini-reactors”. The MeOH from the distillate was recycled and combined with the feed MeOH and then refluxed back to the RD column. The product mixture was withdrawn from the reboiler to a GLY-FAME separator, where the GLY and FAME were separated by gravity in a continuous process. According to He et al. [44], the in-line static mixer served as a pre-reactor in the presence of the reactants and alkali catalyst. This will handle a substantial part of the reaction, which greatly enhances the RD process.

Furthermore, the portion of the recycled MeOH created a high local MeOH:oil ratio and drove the transesterification reaction in the “mini-reactor” toward completion. As a result, the conversion rate and the yield were increased to 95.1% and 94.4% respectively when the MeOH:oil molar ratio of 4:1 was used. By comparing the alcohol usage in the process, the conventional process is still using 100% (by molar quantity) or more excess alcohol [45,46] while the use of alcohol in the RD column has cut down by 66%. This implies that the downstream alcohol recovery effort and the operating cost of the RD column would be reduced by two-third. In addition, the overall liquid retention time in the RD column system was only about 3 min but the retention time of conventional batch or continuous-flow reactors was 60–90 min [47–49]. As a result, the short reaction time in RD column has led the biodiesel production to a higher productivity. Though this RD reactor is more advantageous than conventional batch and continuous-flow biodiesel processes, further investigations are necessary to achieve the complete conversion of the oil and increase the yield productivity of the RD column system.

3.2. Centrifugal contact separator

Centrifugal contact separator (CCS) is another technique, which integrates reaction and centrifugal separation into a single apparatus. CCS is one of the well-known examples of PI. Recently, the use of the centrifugal reactor/separator and CCS (model CINC V02 as shown in Fig. 3) for biodiesel synthesis was reported by McFarlane et al. [50] and Kraai et al. [51] respectively. According to Kraai et al. [51], the CINC V02 (Fig. 3) is a rotating centrifuge in a static reactor housing and operating in a once-through mode for both liquid phases (light phase and heavy phase) without recycle of the exit streams. Pure sunflower oil (preheated to 60 °C) was first fed into the CCS. The reaction was started by feeding the MeOH and sodium methoxide (NaOMe) solution (preheated to 60 °C) at 6:1 molar ratio of MeOH:oil into the CCS. Both

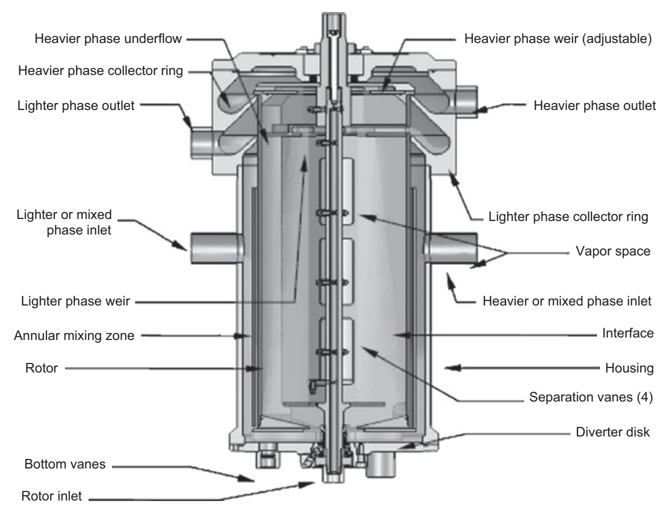


Fig. 3. Schematic diagram of cross-sectional view of the CCS (courtesy of Auxill, the Netherlands) [51].

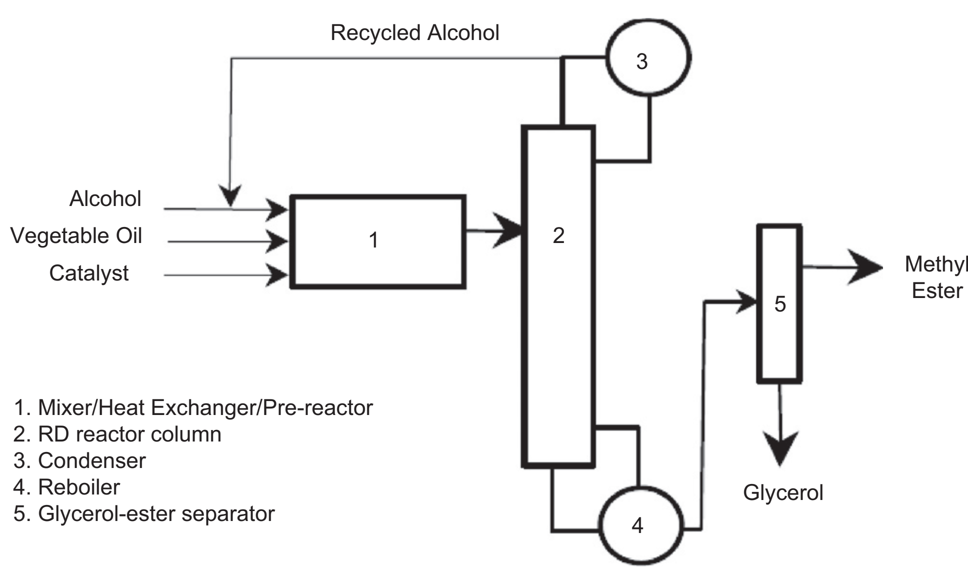


Fig. 2. Biodiesel production process with reactive distillation column [44].

immiscible liquids were dispersed in the annular zone between the static housing and the rotating centrifuge. The dispersion was then transferred into the hollow centrifuge, through a hole in the bottom plate, where phases were separated by centrifugal forces into light and heavy phases. After the reaction achieved the steady state, the GLY with unreacted MeOH flowed out of the heavy phase outlet while the FAME with unreacted oil flowed out of the CCS through the light phase exit. Since the homogeneous catalyst (NaOMe) was used in the reaction, the dissolved catalyst, unfortunately, was present in both outlet phases. As a result, products refining or purification process is necessary.

As reported by Kraai et al. [51], at optimum conditions (rotational frequency, *N*:30 Hz, oil flow rate:12.6 mL/min, NaOMe:1 w/w% of oil, reaction temperature, T:75 °C), the steady state FAME yield of 96% was achieved after about 30 min of reaction time in the CCS (CINC V02). According to a report written by Gerpen et al. [52], some conventional batch processes used a two-step reaction, with glycerol removal between the steps, to increase the final extent of reaction to above 95% at typical reaction time range from 20 minutes to more than one hour. Thus, this appears that the yield productivity of CCS (CINC V02) is at least comparable and likely higher than the conventional batch processes. Several ways have also been tried out in order to enhance the FAME yield productivity such as by increasing the reaction temperature, using higher catalyst dosage, adjusting oil feed flow rate and CCS rotational frequency [51]. Due to the excessive MeOH evaporation at high temperature and solid soap formation in the centrifuge (due to higher intakes of catalyst), yield enhancement is impossible by increasing the reaction temperature or using higher catalyst dosage. The FAME yield drops when the oil feed flow rate increases due to the reduction of mean residence times of both phases (light and heavy) in the CCS, thus resulting in lower conversion. However, further reduction of feed flow rate is also not feasible due to the incomplete phase separation of both outlet phases (light and heavy).

On the other hand, the FAME yield increased with increasing *N* up to a maximum between 30 Hz and 40 Hz [51]. A further increase in *N* leads to lower FAME yield. The increase of FAME yield is likely over the formation of small droplets in the annular zone and the high value of volumetric mass transfer coefficient. However, the FAME yield decreased at higher *N* values ($N > 40$ Hz) [51]. In the CCS, this biphasic transesterification reaction with relatively fast kinetics only takes place in a dispersion which is found in the annular zone as well as in some parts of the centrifuge. The volume of the dispersed phase in the annular zone is independent of *N* while the volume of the dispersed phase in the centrifuge is expected to be a function of *N*. According to Kraai et al. [51], the settling velocity of the droplets at the dispersed zone of the centrifuge is proportional to the difference in density, the angular momentum and the squared drop diameter. Therefore, owing to the proportionality of the settling velocity with the angular momentum, it is expected that the dispersed phase volume in the centrifuge will be reduced considerably at high *N* (eg., $N > 40$Hz). As a result, by considering the strong reduction of the dispersed phase volume in the centrifuge, the FAME yield will be reduced at $N > 40$ Hz.

Based on the review on the CCS as discussed earlier, several concerns need to be considered. In order to apply this technology to the industrial scale for biodiesel production, modifications on the CCS are likely needed to achieve higher conversion and yield productivity. In the single-pass operation of CCS, the presence of the side product of GLY will hinder a complete conversion due to the reversible nature of transesterification reaction. Significant improvement in conversion and yield could be achieved by using multi-pass operation with two or three CCSs setup in series. In this manner, the product and unreacted oil from the first and second stages are separated from the GLY so that the forward reaction can be enhanced. The third stage can be used for subsequent aqueous wash to remove the remaining GLY and catalyst. To date, only high purity of vegetable oils (sunflower oil [51]and soybean oil [50]) were used in the CCS for biodiesel synthesis. It is suggested that the CCS can be modified to adapt various feedstocks with a wide range of FFA content. The excess MeOH into the CCS can be recycled to reduce the molar ratio of oil:MeOH, and thus further reduce the overall production costs.

3.3. Membrane reactor

In order to overcome the conventional batch and continuous-flow biodiesel production challenges, membrane reactor technology is developed for a continuous transesterification reaction process. Membrane reactors have several advantages over conventional reactors [53]. A membrane reactor allows reaction and separation to happen within a chamber [54]. The membrane reactor ensures the reversible reaction proceeds rapidly towards the favourable path by removing the reacted products simultaneously, thus leading to high product yields [53,55]. In addition, the membrane reactor can perform a selective separation resulting in only desired products will be filtered out from the reactants. Recently, the two-phase membrane reactor technology for simultaneous transesterification and separation to produce high quality biodiesel receives great attentions. Dube et al. [56], Cao et al. [57–59], Tremblay et al. [60], Badenes et al. [61] and Baroutian et al. [62] have reported on the production of biodiesel using the membrane reactor.

The idea of using membrane reactor for biodiesel production was first proposed by Dube et al. [56] and ever since then, quantitative researches were largely conducted. A schematic diagram of the biodiesel membrane reactor system is shown in Fig. 4. The membrane reactor is mainly operated by exploiting the immiscibility of the oil and MeOH which posed the major mass-transfer limitation to conventional biodiesel production [56]. Considering the immiscibility of oil and MeOH as well as various surface forces, the oil exists in the form of emulsion (droplets suspended in MeOH phase) and transesterification occurs at the surface of the oil droplets. The oil droplets are too large to pass through the permeable membrane while the FAME which solubilized in MeOH (with its smaller molecular size) passes through

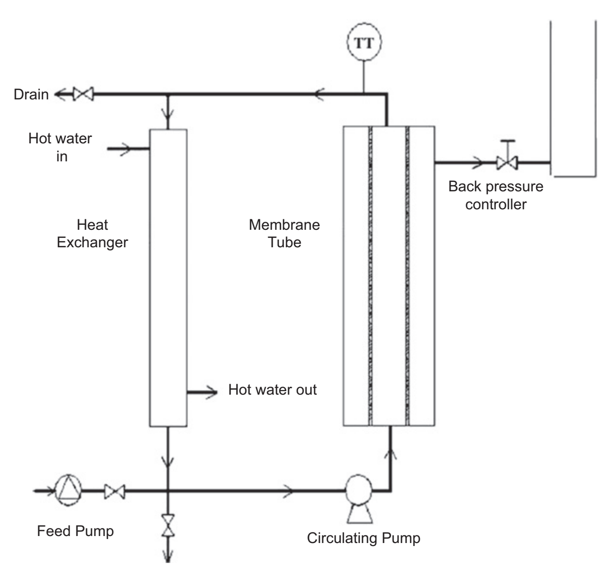


Fig. 4. Schematic diagram of the membrane reactor [56].

the membrane along with the MeOH, GLY and catalyst. In view of this, it is crucial to maintain a separate lipid phase within the membrane reactor system so that high-quality biodiesel production with the negligible amount of TG is insured [58]. In addition, as the transesterification is a reversible reaction, using membrane reactor to remove the products simultaneously from the reactants enhances the reaction rates and thus gives a pure permeate stream, which requires only simple distillation step to obtain biodiesel at high purity.

Cao et al. [58] investigated on various lipid feedstocks with different FFA contents such as soybean oil, canola oil, a hydrogenated palm oil/palm oil blend, yellow grease and brown grease in biodiesel production using a membrane continuous membrane reactor. Results showed that all tested lipid feedstocks with different FFA contents were successfully transesterified in the continuous membrane reactor. Good performance was observed with the quality of FAME produced from each feedstock meeting the ASTM D6751 standard. In addition, the glycerine content in the product stream was significantly lower than that produced by a conventional batch reaction. On the other hand, Cao et al. [57] studied on MeOH recycling in the production of biodiesel using the membrane reactor. In the study, the permeate stream of the membrane reactor was separated at room temperature into a FAME-rich non-polar phase and a MeOH-GLY-rich polar phase. The polar phase was recycled at three recycle ratio: 50%, 75% and 100% at the similar operating conditions. At 100% recycle ratio, the result showed that FAME concentration ranged from 85.7 to 92.4 wt% in the FAME-rich non-polar phase was obtained whereby the overall molar ratio of MeOH:oil in the reaction system was significantly reduced to 10:1. Thus, the reduction in the overall molar ratio of MeOH:oil in the system has saved the cost of downstream MeOH recovery from the product. In short, the membrane reactor used for biodiesel production allows flexible feedstock with efficient separation and purification so that less water washing steps required. Therefore, the membrane reactor is not only considered as time, energy and cost effective but also more environmental friendly.

3.4. High-frequency magnetic impulse cavitation reactor

A module based on cavitation technology, "High-Frequency Magnetic Impulse Cavitation Reactor" was developed to overcome the shortcomings of the conventional technologies for biodiesel production. The inventor of this module, SPECIAL TECHNOLOGIES (Science and Production Association) [63] declared that it is currently the most state-of-the art biodiesel production technology. The module consists of four parts, which are mounted on a single basement with vibratory bearings and is very suitable to be used as a mobile unit. The parts are:

(i) BIOTRON-ST (Fig. 5(a)): consists of electronic precise volumetric dosing system
(ii) PPS-ST 1200 (Fig. 5(b)): chamber of source components pre-mixing,
(iii) PULSAR-ST 215-B (Fig. 5(c)): the third-generation magnetic-impulse cavitation reactor
(iv) Separation with electronic tracking system (Fig. 5(d))

The PULSAR-ST 215-B developed by SPECIAL TECHNOLOGIES is a third-generation hydrodynamic high-frequency magnetic impulse cavitation reactor for biodiesel production [63]. The reactor is the core element of BIOTRON-ST and it has a high level of reliability with modern design and process automation, stable results with any oil types, and minimum power consumption. According to the company of BioFluidTech [64], the high frequency magnetic impulse cavitation differs from the usual cavitation effect with the influence of magnetic field on micro-plasma formations due to active cavitation.

In high-frequency magnetic impulse cavitation, reaction takes place in the reactor on a molecular level. The cavitation caused

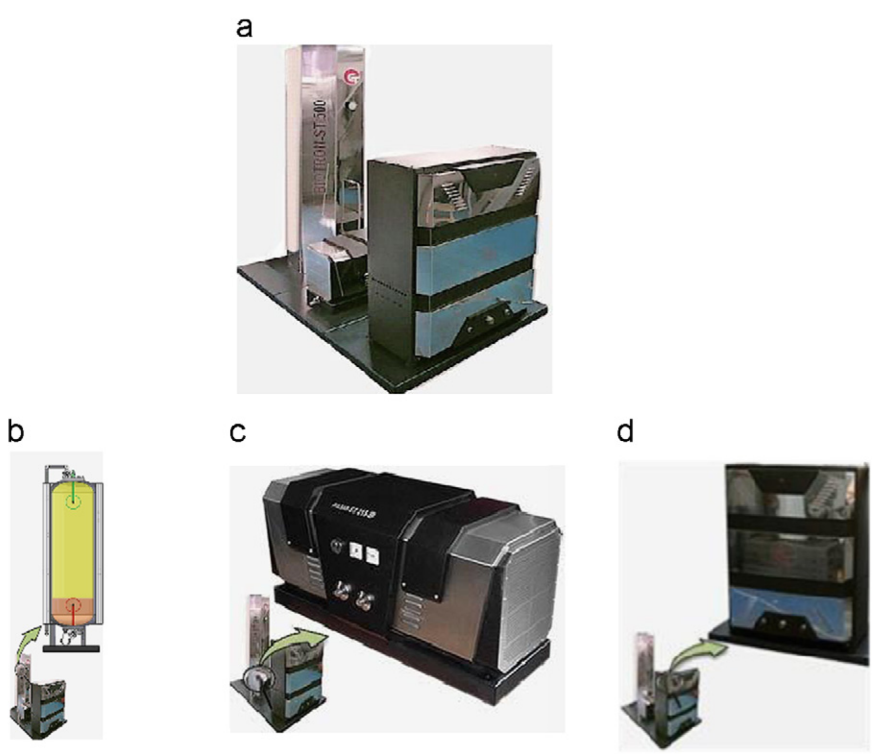


Fig. 5. Diagram of automatic module developed by SPECIAL TECHNOLOGIES (Science and Production Association) for biodiesel production [63]. (a) automatic module BIOTRON-ST. (b) Electronic tracking system. (c) PULSAR-ST 215-B. (d) PPS-ST 1200.

radicalization of the molecules. The oil is characterised not only by the composition of the compounding hydrocarbons but also by the van der Waals interaction between the molecules, which gives oil elastic polymer-like structure that of high viscosity. By using this reactor, all components are exposed to magnetic-directed cavitation pulses. Fatty acid molecules are split using micro-explosions, which results in a decrease of viscosity, an increase of the cetane number and thus leading to an improvement in the energetic parameters of the resulted fuel [63]. Furthermore, the locally increased temperature in collapsing bubbles and the availability of radicals accelerate the transesterification reaction and thus improving the biodiesel product quality.

On the other hand, PPS-ST 1200 is an electronic system used for the preliminary dosing and processing of finished products such as biodiesel and GLY. The system is designed to give steady dosing of source ingredients (oil, alcohol and catalyst) even if ambient conditions vary and has an extremely high dosing precision of about 0.1%. In addition, the electronic tracking system of the module is used to oversee the filling, separation and discharge of finished products whereby supersensitive sensors are used to monitor the state of the GLY and biodiesel in the separation tank in order to eliminate the human factor in evaluating the readiness of the reacted products for subsequent separation.

The high frequency magnetic impulse cavitation reactor has claimed to work well with both crude and refined oil as well as waste vegetable oil with almost any acid number [65]. However, the allowable FFA content presents in the feedstock should be mentioned specifically because the FFA content mainly depends on the nature of feedstock. For instance, waste vegetable oils consist of varying levels of FFA content. It can be less than 15% for yellow grease but exceeds 15% for brown grease [66]. Moreover, the yields of biodiesel and glycerol are not mentioned in any of the studies. It is reported that high-frequency magnetic impulse cavitation technology requires only minimal catalyst quantity and the amount of alcohol consumed in the reaction conforms precisely to the minimum volume required based on the stoichiometry composition. Therefore, conventional alcohol recovery process is not required. In addition, products purification or refinery process involving water washing could be eliminated because only a simple ion exchange filtering step is required to polish the finished product.

3.5. Ultrasonic cavitation reactor

Lately, the use of ultrasound has gained interest in biodiesel production. Ultrasonic wave (ultrasound) is a sound wave having a frequency higher than human audibility limits [67]. Ultrasound provides the mechanical energy for mixing and the required activation energy for initiating the transesterification reaction [68]. Thence, the reaction time is shortened, and the biodiesel yield is increased [69–72]. The ultrasound phenomenon has its physical and chemical effects on the liquid-liquid heterogeneous reaction system through cavitation bubbles following the principles as follows [73]: (1) the chemical effect, in which radicals such as H+, OH-, and H02+ are produced during a transient implosive collapse of bubbles (in a liquid irradiated with ultrasound) that accelerate chemical reaction in the bulk medium; (2) the physical effect of emulsification, in which the micro-turbulence generated due to radial motion of bubbles, creates an intimate mixing (homogenise the mixture) of the immiscible reactants. Considering all these principles, the interfacial region between the oil and alcohol intensively increases, resulting in faster reaction kinetics and higher conversion of oil and product yield.

The ultrasonic reactor was first introduced by Hielscher Ultrasonics GmbH for biodiesel production in the early 2000s. The Hielscher ultrasonic reactor adopts an ultrasonic processor, which operates at an ultrasonic frequency ranged from 18 to 20 kHz. Ultrasonic waves at this frequency create an intense cavitation in liquids. The collapse of the cavitation bubbles creates emulsification of immiscible liquids. Stavarache et al. [15,74] have investigated the transesterification of vegetable oil using low-frequency ultrasound (28–40 kHz). An excellent yield (≈ 98%) was obtained at a 28 kHz ultrasound while a significant reduction of reaction time was obtained by using a 40 kHz ultrasound. Colucciet. al. [75] hypothesised that the observed mass transfer and kinetic rate enhancements were mainly caused by the increase in interfacial area and activity of the microscopic and macroscopic bubbles formed when ultrasonic waves of 20 kHz were applied to the two-phase reaction system.

According to Hielscher Ultrasonics GmbH [76], continuous ultrasonic biodiesel processing and separation can be achieved by first mixing the heated oil with the pre-mixed alcohol and catalyst continuously as shown in Fig. 6. The oil/catalyst mixture is then passed through an inline static mixer to improve the homogeneity of the feed in the ultrasonic reactor. The mixture is directed through the flow cell, where it will be exposed to ultrasonic cavitation for about 5–30 s. After that, the sonicated mixture enters the reactor column which is designed to give approximately one hour of retention time for the transesterification reaction to be completed. The biodiesel and glycerine products were separated in the centrifuge. It is then followed by the continuous products' post-treatment steps for alcohol recovery, product washing and drying.

It is important to note that the processing time is reduced to less than 30 seconds, and the separation time is reduced to less than 60 min by using the ultrasonic reactor. The ultrasonic reactor is also capable to deliver a biodiesel yield in excess of 99% [76] at a reduced amount of catalyst and MeOH required in the reaction. Furthermore, Hielscher ultrasonic reactor shows outstanding energy efficiency, when compared to high-shear mixing and hydrodynamic cavitation. The Hielscher ultrasonic reactor requires approx. 1.4 kWh/m^3 for biodiesel production. However, the hydrodynamic magnetic impulse cavitation requires approximate 32.0 kWh/m^3 and the high-shear mixing requires approximate 4.4 kWh/m^3 [77] to achieve the similar result.

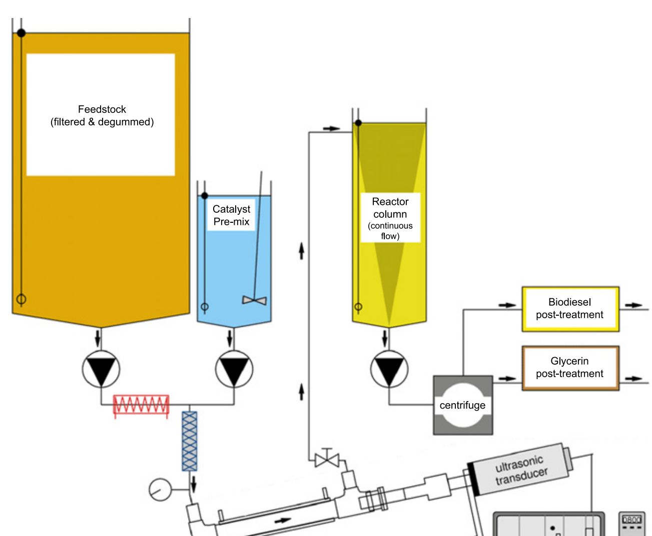


Fig. 6. Hielscher continuous ultrasonic biodiesel processing and separation setup [76].

Table 5
Comparison between the main features of commercial technologies and PI methods for biodiesel production.

		Feedstock	Product(s) quality	Environmental impact	Main features of the technology	Reference
Commercial biodiesel enterprises(Conventional methods)	Pacific Biodiesel	(i) Multi-feedstock flexibility (ii) With pre-treatment unit, raw material with high content of FFA (up to 15%), like animal fats, used oils and greases can be used as feedstock	(iii) Produce fuel quality meets the ASTM D6751-07a standards (iv) The resulting glycerine at the purity of more than 85% is upgradable to United States Pharmacopeia quality (v) However, amount of conversion of oil to biodiesel and the yield productivity are still questionable	(vi) Dry refining process developed by Pacific Biodiesel uses no water and provides consistently high quality biodiesel (vii) The use of a three-step recovery system leads to low consumption of methanol (viii) Less hazardous waste water produced and resolves waste treatment problem	(ix) Use waterless semi-batch homogeneous transesterification process for biodiesel production (x) Consists of three stage product refining, vacuum distillation and dry refining steps	Pacific Biodiesel, I. [21], [26]
	Lurgi	(xi) Multi-feedstock flexibility (xii) Animal fats, used oils, greases, oil with high content of FFA can be used as feedstock	(xiii) The biodiesel yield can achieve 100% while the quality of biodiesel meets the European and/or US ASTM standards (xiv) Glycerine with concentration up to 80% can be further purified to produce a EU Pharmacopeia standard glycerine	(xv) Approximate 20 kg of water used for subsequent counter-current washing step to remove by-product components (xvi) Surplus methanol is removed from the glycerine and water phases (xvii) The surplus methanol is recycled back to the process (xviii) Minimal waste generation	(xix) Homogeneous transesterification takes place in a dual reactor system, which operating with a patented glycerine cross flow configuration for maximised conversion (xx) The system involves phase separation by gravity process (no centrifuge needed)	GmbH, L. [27]
	Desmet Ballestra	(xxi) Multi-feedstock flexibility (xxii) With the pre-treatment unit, oil with a maximum 5% of FFA such as animal fats, used oils and greases can be used as feedstock	(xxiii) Glycerine with concentration up to 90% can be further purified to produce a EU Pharmacopeia standard glycerine	(xxiv) The purification process involves separation of unreacted methanol, washing with citric acid and water solutions (xxv) Waste water is generated in the refining step	(xxvi) The system consists of continuous three steps homogeneous transesterification reaction section with state-of-the-art technology for multiple glycerine separation (xxvii) Easy and accurate dosing of reactants (xxviii) Glycerine recuperation at each reaction step (xxix) Limited product hold-up	Oleo, D.B. [22]

Table 5 (*continued*)

		Feedstock	Product(s) quality	Environmental impact	Main features of the technology	Reference
	Axens Technologies	(xxx) Feedstock must consists less than 0.25% of FFA content and water content must be lower than 1000rpm	(xxxi) The biodiesel can be produced at purity exceeds 99% without purification step (xxxii) The product yield is close to 100% (xxxiii) Glycerine can be produced with high purity level, at least 98%	(xxxiv) Excess methanol is removed by partial evaporation and recycled back to the process (xxxv) Remove soluble glycerine using an absorber (xxxvi) No hazardous chemical handling and minimal waste generation (xxxvii) However, the system operates at high temperature and pressure	(xxxviii) The technology involves a continuous heterogeneous catalytic transesterification reaction (xxxix) Use heterogeneous catalyst – a mixed oxide of two (non-noble) metals, in two fixed bed reactors	Melero et al. [24] and Bournay et al. [28]
Process intensification methods	Reactive distillation column	(xl) Canola oil was used as a feedstock	(xli) High conversion rate (95.1%) with no excess alcohol needed in the reaction (xlii) High productivity of biodiesel (94.4% of yield)	(xliii) The methanol from the distillate was recycled and refluxed back to the column	(xliv) The system consists of a combination of the chemical reaction and distillation separations in a single unit (xlv) An in-line static mixer (pre-reactor) enhances the process (xlvi) Low catalyst concentration in the reaction (xlvii) Short reaction time	He et al. [44]
	Centrifugal contact separator (CCS)	(xlviii) Only high purity of vegetable oils (sunflower oil and soybean oil) were used as feedstock (xlix) The CCS can be modified to adapt various feedstocks with a wide range of FFA content	(l) Biodiesel yield of 96% can be achieved after 30 min of reaction in the CCS (li) Multi-pass operation by using two or three CCSs in series could improve the conversion and yield productivity	(lii) Products refining process is needed because of the dissolved homogeneous catalyst (NAaOMe) present in the product phase (liii) The excess methanol can be recycled back to the CCS	(liv) The technology involves an integration of reaction and centrifugal separation into a single apparatus (lv) It eliminates a subsequent liquid-liquid separation step (lvi) The reactor can be operated as mobile unit for biodiesel production	Kraai et al. [51]

Membrane reactor	(lvii) Lipid feedstocks with different FFA contents can be used for biodiesel production	(lviii) The quality of biodiesel produced from various feedstock meets the ASTM D6751 standard (lix) The glycerine content in the product stream was significantly lower than that produced by a conventional batch reaction	(lx) The recycled methanol leads to lower methanol to oil molar ratio in the reaction system (lxi) It gives efficient separation and purification whereby less water washing steps are required	(lxii) A membrane reactor allows reaction and separation to happen within a chamber (lxiii) Mainly operated by exploiting the immiscibility of the oil and methanol and various surface forces (lxiv) Soap formation in the reactor might cause membrane fouling issue	Thomas et al. [54], Dube et al. [56], Cao et al. [58]
High frequency magnetic impulse cavitation reactor	(lxv) It works well with both crude and refined oil and waste vegetable oil with any acid number (lxvi) However, the tolerance limit of FFA contents present in feedstock is not mentioned in any of the studies	(lxvii) The yield of biodiesel and glycerine and product productivity are not clearly mentioned	(lxviii) The system requires only minimal catalyst quantity and the amount of alcohol consumed conforms precisely to the minimum volume required based on the stoichiometry composition (lxix) No alcohol recovery process involved (lxx) Product purification involving water washing could be eliminated	(lxxi) Reaction takes place in the reactor on a molecular level (lxxii) The system is designed to give steady dosing of oil, alcohol and catalyst even if ambient conditions vary (lxxiii) The system uses a high dosing precision of about 0.1% (lxxiv) Electronic tracking system is used to oversee the filling, separation and products discharging	Pierce, [63] and Corporation, [65]
Ultrasonic cavitation reactor	(lxxv) Raw materials of lower quality such as animal fats, recycled restaurant oils or waste oils can be used as feedstocks (lxxvi) The ultrasonic process intensification improves the conversion with using any feedstock (high FFA oil or high viscosity fat or grease)	(lxxvii) The reactor is able to produce a biodiesel yield in excess of 99% (lxxviii) The product is meeting the ASTM D6751or European EN 14212 standards (lxxix) Glycerine produced contains less catalyst and it causes lower refining costs	(lxxx) The amount of catalyst and methanol required in the reaction is reduced by up to 50% (lxxxi) Less hazardous and minimal waste generation	(lxxxii) Ultrasound provides the mechanical energy for mixing and activation energy for initiating the transesterification reaction (lxxxiii) The reaction time is shortened and the separation time is reduced (lxxxiv) The reactor shows outstanding energy efficiency	Singh et al. [68], Hielscher Ultrasonics GmbH [76]

3.6. Comparison between conventional biodiesel technology and PI technology

In the previous sessions, investigation was focused on various operating options of conventional biodiesel technologies and emerging PI technologies available for biodiesel production. The comparison of main features of conventional industrial processes and technologies developed based on PI methods were summarised in Table 5. As seen in Table 5, the quality and the yield of biodiesel are affected by the production methods as well as the choice of raw materials. A variety of oil and fat waste products has been used as the raw material in the industrial biodiesel production and also the emerging PI technologies. Clearly, many of the conventional biodiesel processes/technologies were designed and implemented based on the factors of desired capacity, feedstock type and quality, alcohol and catalyst recovery, products quality and environmental issues. However, a pre-treatment unit is required for refining the low quality feedstock. On the other hand, different approaches have been developed based on PI concept, resulting in different operating requirements, water consumption, operating modes, and operating system limitations. Most importantly, they are capable in handling a variety of feedstocks with different qualities without the pre-treatment process.

It is important to underline that methanol and alkali catalyst are widely used for majority of the biodiesel production for both conventional and emerging PI technologies. This is typically due to the low price of alcohol and catalyst used for optimisation of production costs and the supply of raw lipid materials. Low cost lipid feedstock, alcohol (MeOH) and alkali catalyst (NaOH) are the only realistic options as long as no better benefits can be contributed by using a more costly alternative material for today's biodiesel production. Still, emerging PI technologies such as RD, CCS, membrane reactor, high-frequency magnetic impulse cavitation reactor and ultrasonic cavitation reactor appear to be a cost-effective and environmental friendly operation in comparison with conventional biodiesel production technologies.

4. Conclusion

As shown in the feasibility studies, most of the commercial biodiesel enterprises claimed that oil with high content of FFA can be used for biodiesel production. However, a pre-treatment and/or esterification units are necessary to pre-treat the FFA content feedstock prior to the transesterification process. Besides, water washing refining step is required for removing excess alcohol and catalyst residues, residual of TG, free glycerine and other undesirable products soluble in the biodiesel. In commercial biodiesel processing, longer residence time is needed to achieve a greater extent of reaction. As a result, additional pre- and post-treatment units will incur additional costs to the total manufacturing costs. Notably, recent emerged PI technologies have significantly improved the biodiesel transesterification process. Apart from being more advanced technology, PI technology has given promised advantages over commercial biodiesel process such as feedstock flexibility, homogenisation of reaction, high conversion and product yield as well as environmental friendly. Despite all these advantages, PI technologies could be further improved so that the biodiesel produced will stay competitive economically against the fossil fuel or alternative fuels.

References

[1] Atadashi IM, Aroua MK, Aziz AA. Biodiesel separation and purification: a review. Renewable Energy 2011;36:437–43.
[2] Cheng Sit Foon CYM, Yung Chee Liang, Ngan Ma Ah, Yusof Basiron. Palm biodiesel: gearing towards Malaysian biodiesel standard. Malaysia Palm Oil Board Palm Oil Developments; 2005.
[3] West Conshohocken, PA, USA: American Society for Testing and Materials; 2011 p. 9.
[4] Brussels, Belgium: European Committe for Standardization; 2003.
[5] Ng JH, Ng H, Gan S. Recent trends in policies, socioeconomy and future directions of the biodiesel industry. Clean Technologies and Environmental Policy 2010;12:213–38.
[6] Sharma YC, Singh B. Development of biodiesel: current scenario. Renewable and Sustainable Energy Reviews 2009;13:1646–51.
[7] Rutz D, Janssen R. BioFuel technology handbook. Munchen, Germany: WIP Renewable Energies; 2007.
[8] Hill K, Hofer R. Chapter 9.1 Natural fats and oils1: Sustainable Solutions for Modern Economies. The Royal Society of Chemistry; 2009 p. 167–237.
[9] Shay EG. Diesel fuel from vegetable oils: status and opportunities. Biomass and Bioenergy 1993;4:227–42.
[10] Champaign, IL, USA: American Oil Chemists Society; 2005.
[11] Schwab AW, Bagby MO, Freedman B. Preparation and properties of diesel fuels from vegetable oils. Fuel 1987;66:1372–8.
[12] Ferella F, Mazziotti Di Celso G, De Michelis I, Stanisci V, Vegliò F. Optimization of the transesterification reaction in biodiesel production. Fuel 2010; 89:36–42.
[13] Vicente G, Marti´nez M, Aracil J. Integrated biodiesel production: a comparison of different homogeneous catalysts systems. Bioresource Technology 2004;92:297–305.
[14] Freedman B, Butterfield RO, Pryde EH. Transesterification kinetics of soybean oil 1. Journal of the American Oil Chemists' Society 1986;63:1375–80.
[15] Stavarache C, Vinatoru M, Nishimura R, Maeda Y. Fatty acids methyl esters from vegetable oil by means of ultrasonic energy. Ultrasonics Sonochemistry 2005;12:367–72.
[16] Zhou W, Boocock DGB. Phase behavior of the base-catalyzed transesterification of soybean oil. JAOCS, Journal of the American Oil Chemists' Society 2006;83:1041–5.
[17] Freedman B, Pryde EH. Fatty esters from vegetable oils for use as a diesel fuel. 1982 p. 117–112.
[18] Freedman B, Pryde EH, Mounts TL. Variables affecting the yields of fatty esters from transesterified vegetable oils. Journal of the American Oil Chemists Society 1984;61:1638–43.
[19] Ejikeme PM, Anyaogu ID, Ejikeme CL, Nwafor NP, Egbuonu CAC, Ukogu K, et al. Catalysis in biodiesel production by transesterification processes—an insight. E-Journal of Chemistry 2010;7:1120–32.
[20] Zhang Y, Dubé MA, McLean DD, Kates M. Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis. Bioresource Technology 2003;90:229–40.
[21] Pacific Biodiesel I. Process Technology. Pacific Biodiesel, Inc.; 2011. 〈http://www.biodiesel.com/index.php/technologies/biodiesel_process_technology〉; Last accessed, 8th November, 2011.
[22] Oleo DB Biodiesel Technologies: generating clean & sustainable energy. 2004. 〈http://www.desmetballestrarosedowns.com/brochures.html〉; Last accessed, 8th November, 2011.
[23] Di Serio M, Cozzolino M, Giordano M, Tesser R, Patrono P, Santacesaria E. From homogeneous to heterogeneous catalysts in biodiesel production. Industrial and Engineering Chemistry Research 2007;46:6379–84.
[24] Melero JA, Iglesias J, Morales G. Heterogeneous acid catalysts for biodiesel production: current status and future challenges. Green Chemistry 2009;11: 1285–308.
[25] Kapilakarn K, Peugtong A. A comparison of costs of biodiesel production from transesterification. International Energy Journal 2007;8:1–6.
[26] Pacific Biodiesel I. Biodiesel Process Equipment and Systems. 2011. 〈http://www.biodiesel.com/index.php/technologies/biodiesel_process_equipment_and_systems〉; Last accessed, 8th November, 2011.
[27] GmbH L 1996. 〈http://www.lurgi.com/website/Biodiesel.57.0.html?&L=1〉; Last accessed, 8th November, 2011.
[28] Bournay L, Casanave D, Delfort B, Hillion G, Chodorge JA. New heterogeneous process for biodiesel production: a way to improve the quality and the value of the crude glycerin produced by biodiesel plants. Catalysis Today 2005; 106:190–2.
[29] Ondrey G. Biodiesel production using a heterogeneous catalyst. Chementator: Chemical Engineering 2004.
[30] Karaosmanoğlu F, Cığızoğlu KB, Tüter M, Ertekin S. Investigation of the Refining Step of Biodiesel Production. Energy & Fuels 1996;10:890–5.
[31] C WT, R C. Process intensification: laminar flow heat transfer. Chemical Engineering Research and Design 1986;64:293–301.
[32] Stankiewicz AI, Moulijn JA. Process intensification: transforming chemical engineering. Chemical Engineering Progress 2000;96:22–33.
[33] Stankiewicz A, Drinkenburg AAH Process intensification: history, philosophy, principles. In: Stankiewicz A, Moulijn JA, editors. Re-engineering the chemical processing plant: Marcel Dekker, Inc.
[34] De Lima Da Silva N, Santander CMG, Batistella CB, Filho RM, MacIel MRW. Biodiesel production from integration between reaction and separation system: Reactive distillation process. Applied Biochemistry and Biotechnology 2010;161:245–54.
[35] Estrada-Villagrana AD, Quiroz-Sosa GB, Jiménez-Alarcón ML, Alemán-Vázquez LO, Cano-Domínguez JL. Comparison between a conventional process and reactive

distillation for naphtha hydrodesulfurization. Chemical Engineering and Processing 2006;45:1036–40.
[36] Tuchlenski A, Beckmann A, Reusch D, Dussel R, Weidlich U, Janowsky R. Reactive distillation—industrial applications, process design & scale-up. Chemical Engineering Science 2001;56:387–94.
[37] Morgan WD. Production of biodiesel fuels which are low in glycerin and sulfur. In: Organization WIP, editor. PATENTSCOPE. C10L 1/19 (2006.01) ed. US2008.
[38] Singh AP, Thompson JC, Brian He B. A continuous-flow reactive distillation reactor for biodiesel preparation from seed oils. In: ASAE Annual International Meeting; 2004. p. 6623–33.
[39] Miranda-Galindo EY, Segovia-Hernández JG, Hernandez S, de la Rosa Álvarez G, Gutiérrez-Antonio C, Briones-Ramírez A. Design of reactive distillation with thermal coupling for the synthesis of biodiesel using genetic algorithms. Computer Aided Chemical Engineering 2009:549–54.
[40] Kiss AA, Omota F, Dimian AC, Rothenberg G. The heterogeneous advantage: biodiesel by catalytic reactive distillation. Topics in Catalysis 2006;40: 141–50.
[41] He BB, Singh AP, Thompson JC. Experimental optimization of a continuous-flow reactive distillation reactor for biodiesel production. Transactions of the American Society of Agricultural Engineers 2005;48:2237–43.
[42] Demirbas A. Biodiesel from vegetable oils via transesterification in supercritical methanol. Energy Conversion and Management 2002;43:2349–56.
[43] Chokchai Mueanmas KPaCT. Feasibility study of reactive distillation column for transesterification of palm oils. International Journal of Chemical Engineering and Applications 2010;1:77–83.
[44] He BB, Singh AP, Thompson JC. A novel continuous-flow reactor using reactive distillation for biodiesel production. Transactions of the ASABE 2006; 49:107–12.
[45] Bunyakiat K, Makmee S, Sawangkeaw R, Ngamprasertsith S. Continuous production of biodiesel via transesterification from vegetable oils in supercritical methanol. Energy & Fuels 2006;20:812–7.
[46] Jansri S, Ratanawilai SB, Allen ML, Prateepchaikul G. Kinetics of methyl ester production from mixed crude palm oil by using acid-alkali catalyst. Fuel Processing Technology 2011;92:1543–8.
[47] Prateepchaikul G, Allen ML, Leevijit T, Thaveesinsopha K. Methyl ester production from high free fatty acid mixed crude palm oil. Songklanakarin Journal of Science and Technology 2007;29:1551–61.
[48] Darnoko D, Cheryan M. Kinetics of palm oil transesterification in a batch reactor. Journal of the American Oil Chemists' Society 2000;77:1263–7.
[49] Rashid U, Anwar F. Production of biodiesel through optimized alkaline-catalyzed transesterification of rapeseed oil. Fuel 2008;87:265–73.
[50] McFarlane J, Tsouris C, Birdwell JF, Schuh DL, Jennings HL, Palmer Boitrago AM, et al. Production of biodiesel at the kinetic limit in a centrifugal reactor/ separator. Industrial & Engineering Chemistry Research 2010;49:3160–9.
[51] Kraai GN, Schuur B, van Zwol F, van de Bovenkamp HH, Heeres HJ. Novel highly integrated biodiesel production technology in a centrifugal contactor separator device. Chemical Engineering Journal 2009;154:384–9.
[52] Gerpen JV, Shanks B, Pruszko R, Clements D, Knothe G. Biodiesel production technology. National Renewable Energy Laboratory; 2004.
[53] Armor JN. Applications of catalytic inorganic membrane reactors to refinery products. Journal of Membrane Science 1998;147:217–33.
[54] Thomas S, Hamel C, Seidel-Morgenstern A. Basic problems of chemical reaction engineering and potential of membrane reactors. In: Seidel-Morgenstern A, editor. Membrane reactors. KGaA, Weinheim: Wiley-VCH Verlag GmbH & Co.; 2008.
[55] Sirkar KK, Shanbhag PV, Kovvali AS. Membrane in a reactor: a functional perspective. Ind Eng Chem Res 1999;38:3715–37.
[56] Dubé MA, Tremblay AY, Liu J. Biodiesel production using a membrane reactor. Bioresource Technology 2007;98:639–47.
[57] Cao P, Dubé MA, Tremblay AY. Methanol recycling in the production of biodiesel in a membrane reactor. Fuel 2008;87:825–33.
[58] Cao P, Dubé MA, Tremblay AY. High-purity fatty acid methyl ester production from canola, soybean, palm, and yellow grease lipids by means of a membrane reactor. Biomass and Bioenergy 2008;32:1028–36.
[59] Peigang C, Tremblay AY, Dubé MA, Morse K. Effect of membrane pore size on the performance of a membrane reactor for biodiesel production. Industrial and Engineering Chemistry Research 2007;46:52–8.
[60] Tremblay AY, Cao P, Dube´ MA. Biodiesel production using ultralow catalyst concentrations. Energy & Fuels 2008;22:2748–55.
[61] Badenes SM, Lemos F, Cabral JMS. Performance of a cutinase membrane reactor for the production of biodiesel in organic media. Biotechnology and Bioengineering 2011;108:1279–89.
[62] Baroutian S, Aroua MK, Raman AAA, Sulaiman NMN. A packed bed membrane reactor for production of biodiesel using activated carbon supported catalyst. Bioresource Technology 2011;102:1095–102.
[63] Pierce E Biodiesel Production Equipment. 2010. 〈http://www.specialtechnologies.eu/en/biodiesel_production_equipment/〉; Last accessed, 8th November, 2011.
[64] Carew B Automatic Modules for Biodiesel Production BIOSTRIM. 2007. 〈http://www.biofluidtech.com/auto.html〉; Last accessed, 8th November, 2011.
[65] Corporation T. BD70 Introduction. Eco-Fusion, Inc.; 2007. 〈http://eco-fusion.ca/biodisel_introduction.html〉; Last accessed, 8th November, 2011.
[66] C M, VG J. Biodiesel production from oils and fats with high free fatty acids. Transactions of the American Society of Agricultural Engineers 2001;44: 1429–36.
[67] Mason TJ, Lorimer PJ. Sonochemistry: theory, applications & uses of ultrasound in chemistry. John Wiley & Sons; 1988.
[68] Singh AK, Fernando SD, Hernandez R. Base-catalyzed fast transesterification of soybean oil using ultrasonication. Energy & Fuels 2007;21:1161–4.
[69] Deshmane VG, Gogate PR, Pandit AB. Ultrasound-assisted synthesis of biodiesel from palm fatty acid distillate. Industrial & Engineering Chemistry Research 2008;48:7923–7.
[70] Armenta R, Vinatoru M, Burja A, Kralovec J, Barrow C. Transesterification of fish oil to produce fatty acid ethyl esters using ultrasonic energy. Journal of the American Oil Chemists' Society 2007;84:1045–52.
[71] Stavarache C, Vinatoru M, Maeda Y. Ultrasonic versus silent methylation of vegetable oils. Ultrasonics Sonochemistry 2006;13:401–7.
[72] Hanh HD, Dong NT, Okitsu K, Nishimura R, Maeda Y. Biodiesel production through transesterification of triolein with various alcohols in an ultrasonic field. Renewable Energy 2009;34:766–8.
[73] Kalva A, Sivasankar T, Moholkar VS. Physical mechanism of ultrasound-assisted synthesis of biodiesel. Industrial & Engineering Chemistry Research 2008;48:534–44.
[74] CS MV, Nishimura R, Maeda Y. Conversion of vegetable oil to biodiesel using ultrasonic irradiation. Chem Lett. 2003;32:716–7.
[75] Colucci J, Borrero E, Alape F. Biodiesel from an alkaline transesterification reaction of soybean oil using ultrasonic mixing. Journal of the American Oil Chemists' Society 2005;82:525–30.
[76] Hielscher T Ultrasonic processors for biodiesel production. Hielscher Ultrasonics GmbH; 1999. 〈http://www.hielscher.com/ultrasonics/biodiesel_transesterification_01.html〉; Last accessed, 8th November, 2011.
[77] Hielscher T Ultrasonicatin saves energy and costs. Hielscher Ultrasonic GmbH; 1999. 〈http://www.hielscher.com/ultrasonics/energy_efficiency_01.html〉; Last accessed, 8th November, 2011.
[78] Agarwal AK. Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. Progress in Energy and Combustion Science 2007;33(3):233–71.
[79] Al-Zuhair S. Production of biodiesel: possibilities and challenges. Biofuels, Bioproducts and Biorefining 2007;1(1):57–66.
[80] Ma F, Hanna MA. Biodiesel production: a review. Bioresource Technology. 1999;70(1):1–15.
[81] Fukuda H, Kondo A, Noda H. Biodiesel fuel production by transesterification of oils. Journal of Bioscience and Bioengineering 2001;92(5):405–16.
[82] Helwani Z, Othman MR, Aziz N, Fernando WJN, Kim J. Technologies for production of biodiesel focusing on green catalytic techniques: a review. Fuel Processing Technology 2009;90(12):1502–14.
[83] Taher H, Al-Zuhair S, Al-Marzouqi AH, Haik Y, Farid MMA. Review of enzymatic transesterification of microalgal oil-based biodiesel using supercritical technology. Enzyme Research 2011:1–25.
[84] Sharma YC, Singh B, Upadhyay SN. Advancements in development and characterization of biodiesel: a review. Fuel 2008;87(12):2355–77.
[85] Robles-Medina A, Gonzalez-Moreno PA, Esteban-Cerdan L, Molina-Grima E. Biocatalysis: towards ever greener biodiesel production. Biotechnology Advances 2009;27(4):398–408.
[86] Sohpal VK, Singh A, Dey A. Fuzzy modeling to evaluate the effect of temperature on batch transesterification of *Jatropha curcas* for biodiesel production. Bullentin of Chemical Reaction Engineering & Catalysis 2011; 6(1):31–8.
[87] Demirbas A. Progress and recent trends in biofuels. Progress in Energy and Combustion Science 2007;33(1):1–18.
[88] Shahid EM, Jamal Y. Production of biodiesel: a technical review. Renewable and Sustainable Energy Reviews 2011;15:4732–45.
[89] Atadashi IM, Aroua MK, Abdul Aziz A. High quality biodiesel and its diesel engine applicatin: a review. Renewable and Sustainable Energy Reviews 2010;14(7):1999–2008.